Hydrophobic and Oleophobic Coatings Based on Perfluoropolyether/Silica Hybrids by the Sol-Gel Method

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ABSTRACT: Glass substrates were spin-coated with a perfluoropolyether oligomer based organic-inorganic hybrid material, and prepared by the sol-gel process. Contact angle analysis and atomic force microscopic analysis were carried out to characterize the surface of the prepared coatings. All systems exhibited strong hydrophobic and oleopophobic characteristics. The wettability behavior was found to be almost independent of both molecular weight and functionality of the fluorinated oligomer. The low values obtained for the contact angle and surface tension indicate that surface segregation of perfluoropolyether

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segments is likely to take place within the network. On the basis of these results and the high quality of the obtained coatings, these materials could be used as functional coatings to impart water and oleo-repellent characteristics to glasses and other similar substrates. © 2008 Wiley Periodicals, Inc. Adv Polym Techn 27: 1–9, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/adv.20098

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Introduction

In the last decade, organic-inorganic (O-I) hybrid materials (also known as ceramers) have attracted steadily growing interest owing to their peculiar and fascinating characteristics derived from an easy control of the final properties by a suitable balance of the properties of each component. In principle, several strategies can be adopted for the preparation of these materials, i.e., the incorporation of inorganic structures on a nanometric scale in polymers through the in situ formation of an inorganic network, the incorporation of preformed dense inorganic structures (clusters or particles), the formation of hybrids using porous or layered inorganic materials, either by interpenetration of the organic polymers into the voids or by exfoliation of the inorganic material.[1]

O-I hybrids are characterized by a remarkable enhancement in properties such as mechanical, thermal, electrical, and magnetic properties in comparison with pure organic polymers. Several commercial applications have already been developed for this kind of hybrids materials, in particular protective coatings on both organic and inorganic substrates.[2]

One of the preferred synthetic methods employed to prepare these materials is the sol–gel process.[3] The classical sol-gel process consists of a two-step hydrolysis-condensation reaction starting with metal alkoxides $M(OR)_x$, typically tetraethoxysilane. The presence of an organic oligomer or polymer in the reactive system, bearing suitable functional groups that are reactive toward the other reactants of the sol-gel process, leads to the formation of covalent bonds between organic and inorganic components that are typically phase separated on a nanometric scale.

It is well known that the final morphology of these hybrid materials, and thus their physical properties, is strictly dependent on the characteristics of the organic polymer, such as its molecular weight and its solubility in the sol-gel solution, as well as the presence of reactive functionalities and their associated chemical reaction rates. Other parameters such as phase separation, solvent evaporation rate, and sample thickness also play an important role.

In the present study, the organic component was based on a commercial perfluoropolyether (PFPE)[4–8] that presents the typical properties of fluoropolymers.[9] In particular, PFPE are characterized by very low glass transition temperature (about −120°C), high thermal stability, chemical inertness and solvent resistance, barrier properties, low coefficient of friction, hydrophobicity and lipophobicity, and, in particular, very low surface energy. Depending on the molecular weight and intrinsic structure, the surface tension of linear PFPE systems varies in the range from 14 to 25 $mN \cdot m^{-1}$. These values are at least 10 to 15 $mN \cdot m^{-1}$ lower than those reported for other conventional polymers, with the only exception of polysiloxane.[10] Furthermore, PFPEs are extremely non-polar substances and their very low solubility parameters lead to a marked thermodynamic incompatibility with most common organic polymers and solvents. For this reason, pure PFPE cannot be directly used in the sol-gel process because of the impossibility of finding a common solvent for the fluorinated oligomer and the other reactants (tetraethoxysilane and water). Some investigations regarding the compatibilization of PFPE/silica have already been reported by Mascia et al.[11–15] through the pre-reaction of hydroxy-terminated PFPE with chlorendic anhydride and caprolactone. In the present article, we have modified the PFPE oligomer by preparing block copolymers containing terminal polycaprolactone segments that are soluble in solvents commonly used in sol-gel processes. Previously reported X-ray photoelectron spectroscopic studies carried out on these system[16,17] have shown that the fluorinated

segments of poly(caprolactone-*b*-perfluoropolyether-*b*-caprolactone) (PCL-PFPE-PCL) triblock copolymers tend to migrate to the outer surface owing to the strong thermodynamic driving force to minimize the surface energy. The same behavior was also noted in the case of polymer blends,[18,19] and thus a similar mechanism of surface segregation is expected in the case of PFPE-containing hybrid materials that can potentially be used as functional coatings exhibiting water- and oleo-repellent coatings for glasses and other substrates. To the best of our knowledge, only a few examples have been reported for the preparation of hydrophobic and oleophobic materials obtained by sol-gel approach.[20–22] In particular, the use of PFPE for the preparation of O-I hybrids by using the sol-gel process was reported by Wojcik and Klein[23] who prepared transparent and water-repellent O-I hybrids based both on PFPE diol diacrylate and on perfluoroalkylsilane.

In previous studies,[24,25] we have reported the preparation and the surface characterization, by contact angle measurements, atomic force microscopy, and X-ray photoemission spectroscopy, of O-I hybrids prepared with tetraethoxysilane- and alkoxysilane-terminated PCL-PFPE-PCL block copolymers (molecular weight of PFPE segments-2200 g·mol^{-1}) having an organic phase content ranging from 5%wt to 80%wt. The wettability behavior of the final materials was found to be almost independent of the ratio of organic-to-inorganic components, which implies that the extent of surface segregation of the fluorinated PFPE segments was, in all cases, high enough to give a very highly hydrophobic character to the coating surface.

Since the surface tension of the PFPE oligomers examined varies as a function of their molecular weight, the length of the PFPE segment in a block copolymer may be expected to play an important role with respect to the surface segregation of the fluorinated component, and thus to the wettability (hydrophobicity and oleophobicity) of the resulting hybrid material.

In the present work, we have investigated the surface properties of O-I hybrids prepared with tetraethoxysilane- and alkoxysilane-terminated PCL-PFPE-PCL block copolymers in which the molecular weight of the PFPE segment was varied from 1190 to 3100 g·mol^{-1}. A PFPE-PCL diblock copolymer, having alkoxysilane reactive groups present at one chain end only, was also prepared and used for comparison.

Experimental

MATERIALS

α,ω-Triethoxysilane-terminated poly(caprolactone-*b*-perfluoropolyether-*b*-caprolactone) triblock copolymers were prepared starting from three commercial products supplied by Solvay Solexis[26]: these were respectively the α,ω-hydroxy-terminated perfluoropolyether Fluorolink® E 10 (having molecular weight of 1190 g·mol^{-1} and a polydispersity index of 1.2) and two grades of Fomblin® Z-DOL TX (having molecular weight of 2200 and 3100 g·mol^{-1} and polydispersity index of 1.6 and 1.4, respectively). The average hydroxyl end-group functionality of both Fluorolink® E 10 and Fomblin® Z-DOL TX is 1.92.

α,ω-Hydroxy-terminated poly(caprolactone-*b*-perfluoropolyether-*b*-caprolactone) triblock copolymers were prepared by ring-opening polymerization of caprolactone using Fluorolink® E 10 or Fomblin® Z-DOL TX as transfer agents and in the presence of tin(II) octoate as catalyst. Triethoxysilane end-capping was obtained by bulk reaction with 3-isocyanatopropyltriethoxysilane at 120°C for 3 h according to a previously reported procedure.[24] The materials were coded as TX*x*CL5Si, in which $x = 1, 2, 3$ is a digit denoting the molecular weight of PFPE (1190, 2200, or 3100 g·mol^{-1}, respectively) while 5 represents the number-average degree of polymerization of the short polycaprolactone segments of the copolymer. The molecular structure of the triblock copolymer can be represented by the following formula:

$$(EtO)_3Si\text{-}(CH_2)_3\text{-}NH\text{-}CO\text{-}[O(CH_2)_5\text{-}CO]_5\text{-}(OCH_2CH_2)_nOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2O(CH_2CH_2O)_n[CO\text{-}(CH_2)_5O]_5\text{-}CO\text{-}NH\text{-}(CH_2)_3\text{-}Si(OEt)_3$$

(which can be represented by the simplified structure: $(EtO)_3Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si(OEt)_3$).

The constituent $-CF_2CF_2O-$ and $-CF_2O-$ units are randomly distributed along the macromolecular chains at a ratio (p/q) of 0.9 and an average value of n equal to 1.5.

In a similar way, the triethoxysilane-terminated poly(caprolactone-*b*-perfluoropolyether) diblock copolymer was prepared starting from an experimental sample of monohydroxyl-terminated PFPE, supplied by Solvay Solexis, having a molecular

weight of 800 g·mol^{-1} (having polydispersity index of 1.3 and hydroxyl end-group functionality of 1.0). The material was coded as GalCL5Si. The molecular structure of the diblock copolymer can be represented by the following formula:

$$CF_3O(C_3F_6O)_mCF_2CH_2O(CH_2CH_2O)_n$$
$$[CO\text{-}(CH_2)_5O]_5\text{-}CO\text{-}NH\text{-}(CH_2)_3\text{-}Si(OEt)_3$$

(which can be represented by the simplified structure: PFPE-PCL-Si(OEt)$_3$),

where the average values of n and m are 1.5 and 3.5, respectively.

Tetraethoxysilane (TEOS) was purchased from Aldrich, and tetrahydrofuran, ethanol, and hydrochloric acid at 37% concentration were purchased from Carlo Erba. All reagents were used as received without further purification.

PREPARATION OF O-I HYBRIDS

The mixture of TXxCL5Si/TEOS or GalCL5Si/TEOS was dissolved in THF at a concentration of about 20% wt/vol, and then EtOH was added to enhance miscibility of water (which was added to promote hydrolysis). Hydrochloric acid was added as catalyst at the following molar ratios (with respect to ethoxide groups of both TXCL(x)Si or GalCL(x)Si and TEOS): EtO-:EtOH:H_2O:HCl=1:1:1:0.05.

A typical preparation was as follows: 2.0 g of a TXxCL5Si/TEOS mixture was added to 8 ml of THF in a screw-thread glass vial and mixed until a homogeneous solution was obtained. Then EtOH, water, and HCl (37%wt solution) were added under vigorous stirring at room temperature for about 10 min. The closed vial was placed in air-circulating oven at a temperature of 70°C for different times (respectively 1 and 3 h) in order to allow the partial progress of the sol-gel reaction. Then the sol-gel solution was deposited on to microscope glasses (previously cleaned by washing in standard RCA1 solution, consisting of a mixture of NH_4OH:H_2O_2:H_2O = 1:1:5 and rinsed in bi-distilled water) by spin coating, thus obtaining a typical coating thickness of 0.3–0.4 μm. After a period of 30 min at room temperature, some samples were subjected to thermal curing at 100°C for 2 h.

The same experimental conditions were used to prepare a non-fluorinated O-I hybrid (coded as PCLSi/SiO_2) and pure sol-gel silica (coded as SiO_2) as reference materials.

The nominal weight ratio of organic to inorganic components of the final hybrids TXxCL5Si/SiO_2 or GalCL5Si/SiO_2 was 5:95, calculated by assuming the completion of the sol-gel reaction as shown below:

$$Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 + 4EtOH$$
$$(EtO)_3Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si(OEt)_3 + 6H_2O \rightarrow$$
$$(HO)_3Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si(OH)_3 + 6EtOH$$
$$PFPE\text{-}PCL\text{-}Si(OEt)_3 + 3H_2O \rightarrow$$
$$PFPE\text{-}PCL\text{-}Si(OH)_3 + 3EtOH$$
$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$$

CHARACTERIZATION

Spin-coating was carried out by using a Laurell WS-400B-NPP-Lite spin-coater with a spin rate of 3,000 rpm.

Atomic force microscopic analysis was carried out by using a Veeco EnviroScope atomic force microscope.

Contact angle measurements were carried out by using a DataPhysics OCA 20 apparatus. To avoid any surface contamination (both from unreacted fluorinated and non-fluorinated species and unwanted impurities), all specimens were repeatedly washed first with 1,3-bis-trifluoromethyl-benzene (hexafluoroxylene, a specific solvent for PFPE) and then with THF, and carefully dried just before measurement. Dynamic and static contact angle determinations were carried out on two different specimens of the same sample and an average value of contact angle was determined on the basis of at least 20 measurements. Surface tension values were determined by applying the Owens and Wendt method to static contact angle values with water, n-hexadecane, diiodomethane, and dimethylformamide.

Results and Discussion

ATOMIC FORCE MICROSCOPY AND SURFACE MORPHOLOGY

It is well known that the wettability behavior of real surfaces is controlled by both the surface chemical composition and the surface morphology. Both surface roughness and surface heterogeneity strongly affect the contact angle measurements as pointed out by the classical studies of Wenzel[27,28] and Cassie.[29]

It is also well known that surface properties such as hydrophobicity and oleophobicity are enhanced by increasing surface roughness (morphological effect) and by decreasing the surface energy (chemical composition effect). In this respect, Wenzel proposed a theoretical model that describes the contact angle θ' at a rough surface by modifying the classical Young's equation

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

as follows:

$$\cos\theta' = \frac{r\,(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r\cos\theta,$$

where θ is the contact angle of a liquid droplet on a flat surface (Young contact angle), θ' is the contact angle of a liquid droplet on a rough surface, r is the roughness factor (ratio of the actual area of a rough surface to the geometric projected area), and γ_{SL}, γ_{SV}, and γ_{LV} are the interfacial free energies per unit area of the solid-liquid, solid-vapor, and liquid-vapor interfaces, respectively. As a consequence, in the so-called "Wenzel regime" ("rough regime"), the surface free energy of the solid part of a rough surface is r times higher than that of a flat surface, and the hydrophobicity-oleophobicity of a rough surface is increased by the increase of the solid-liquid contact area.

Atomic force microscopic analysis was carried out on the prepared coatings to evaluate the presence of a "Wenzel regime," and thus the contribution of surface morphology to the wettability. In both investigated cases, a very smooth surface was present with root mean square roughness values well below 10 nm. Accordingly to these data, the roughness factor r was approximately unitary, indicating the absence of significant surface roughness. On the basis of these results, the contact angle data discussed in the next section can be considered to be completely unaffected by the surface roughness of these hybrids, and therefore this last parameter can be neglected for the discussion because of the absence of a "Wenzel regime." In other words, the wettability behavior of the investigated hybrids has its origin in the chemical surface composition, and thus from the preferential surface segregation of fluorinated segments.

CONTACT ANGLE MEASUREMENTS

The values of the advancing and receding contact angles with water and static contact angles with *n*-hexadecane measured on TX*x*CL5Si/SiO_2 and GalCL5Si/SiO_2 hybrids coated on to glass substrate after different reaction times are reported in Table I. For comparison, contact angles of glass substrates uncoated or coated with non-fluorinated hybrids (PCLSi/SiO_2 = 20:80) and with completely inorganic materials (SiO_2, from TEOS) are also reported.

From the reported data, it is clear that a significant increase in contact angles of both water and hydrocarbon (*n*-hexadecane) was observed for coatings based on PFPE hybrids. Concerning the fluorinated coatings, a marked influence of the reaction time of the sol-gel reaction before the coating is applied on the substrate (t_r) is clearly evident for all the samples investigated. The reaction time t_r at 70°C was varied from 1 to 3 h in order to verify the effect of the extent of the reaction (i.e., the degree of branching/crosslinking of the hybrid structure) on the translational mobility of TX*x*CL5Si and GalCL5Si polymers, which is expected to mainly contribute in the reduction of surface segregation of the low surface tension PFPE segments before gelation and vitrification.

The data reported in Table I show that (i) for short reaction times before the coating is applied on the glass (t_r = 1 h), the contact angle values are not directly related to the molecular weight of the PFPE segment; (ii) in all cases for the same molecular weight of the PFPE segment, there is a significant decrease in contact angle when t_r is increased from 1 to 3 h; and (iii) the decrease in contact angle is greater, the lower is the molecular weight of the organic oligomer (well evident for both advancing and receding water contact angles, but also present for hydrocarbon static contact angles).

To explain these results, it is necessary to assume that the final contact angle is the result of a surface segregation of PFPE segments, which, in turn, depends on several concomitant phenomena, namely: (a) translational mobility of TX*x*CL5Si and GalCL5Si; (b) segmental mobility of PFPE segments; (c) phase separation of PFPE segments in fluorinated domains; and (d) solvent evaporation rate. Another contribution could be derived from the migration on to the surface of unreacted fluorinated species owing to their low surface energy. In the present case, this possibility can be ignored in view of the careful washing procedure (see Experimental section) applied to the specimens before the contact angle measurements. To illustrate the efficiency of the washing procedure in removing unreacted species, preliminary tests were carried out by preparing glass substrates coated with non-fluorinated hybrid PCLSi/SiO_2 (20:80) containing

TABLE I
Advancing and Receding Contact Angle With Water ($\theta_{H_2O\_ADV}$ and $\theta_{H_2O\_REC}$) and Static Contact Angle With *n*-Hexadecane (θ_{C16H34}) Measured on TX*x*CL5Si/SiO_2, GalCL5Si/SiO_2, PCLSi/SiO_2, and SiO_2

Sample Code	PFPE Molecular Weight (g·mol^{-1})	t_r (h)	$\theta_{H_2O\_ADV}$ (°)	S.D. (°)	$\theta_{H_2O\_REC}$ (°)	S.D. (°)	θ_{C16H34} (°)	S.D. (°)
GalCL5Si/SiO_2	800	1	87.5	0.8	74.6	2.9	50.7	0.8
		3	75.6	1.0	63.6	1.3	43.4	0.7
TX1CL5Si/SiO_2	1190	1	91.0	0.6	76.7	4.4	51.5	0.8
		3	79.5	0.7	70.0	0.6	49.5	0.4
TX2CL5Si/SiO_2	2200	1	95.8	1.6	84.1	1.6	61.3	0.3
		3	87.1	0.9	76.5	1.6	60.3	0.3
TX3CL5Si/SiO_2	3100	1	89.9	0.5	81.9	1.6	61.9	1.0
		3	88.7	1.3	80.6	0.4	62.7	1.0
PCLSi/SiO_2	–	1	60.8[a]	–	–	–	27.2	–
SiO_2, from TEOS	–	1	57.0[a]	–	–	–	24.4	–
Glass substrate	–	–	37.4[a]	–	–	–	12.9	–

t_r: reaction time of the sol-gel reaction before coating application; S.D.: standard deviation.
[a]Static contact angle data.

small amounts (1 wt%) of an unfunctionalized fully fluorinated PFPE (i.e., fluorinated even in the terminal groups, and thus unable to create covalent bonds during the coating consolidation). In particular, these coatings showed a static water contact angle near 80° before washing and of about 67° after the washing treatment.

Since the coating application method (spin coating at 3000 rpm) gives a solution film thickness of about 0.3–0.4 μm, it is reasonable to assume that the evaporation of the solvent has two main effects: an increase of the viscosity of the reaction medium and a change in the miscibility of the reactants present in the solution before application on to the glass substrate. Both the viscosity and the miscibility of the reactants are affected by the extent of reaction (and therefore by the reaction time t_r) before the coating is applied and in particular an increase of viscosity is expected for higher t_r. The dependence of miscibility on the extent of reaction is difficult to visualize in view of the concurrent increase of molecular weight and the conversion of alkoxysilane into silanol groups.

Because of the low surface tension of PFPE segments, there is a driving force for their migration to the air/solution surface. Translation of the overall $(EtO)_3$Si-PCL-PFPE-PCL-Si$(OEt)_3$ chains (and/or the related products formed during reaction) as well as migration by segmental mobility of constrained PFPE segments can contribute to the fluorine enrichment of the surface. Of course, translational mobility is expected to play the main role before gelation, whereas segmental mobility is expected to be the main contribution after crosslinking (when the PFPE segments are expected to be bonded to the inorganic silica network).

Furthermore, the migration rate due to translational mobility is expected to decrease by increasing both the molecular weight of organic oligomer and the viscosity of the medium. However, another important contribution to translational mobility may derive from the miscibility of the $(EtO)_3$Si-PCL-PFPE-PCL-Si$(OEt)_3$ copolymer (and/or the related products formed during reaction) in the medium, which, in turn, is affected by the molecular weight of the copolymer itself. In particular, it is well known that the miscibility strongly increases by decreasing the molecular weight of PFPE from 3100 to 1190 g·mol^{-1}.

The contact angle results (in particular the water contact angles) can be tentatively explained. For $t_r = 1$ h (the system is far from gel point and the translational mobility is expected to play the main role for the PFPE surface segregation), the highest value of contact angle was observed for TX2CL5Si/SiO_2, even though the chain mobility of TX1CL5Si is expected to be higher than that of TX2CL5Si. A lower contact angle can be explained by assuming that in this case the high miscibility of TX1CL5Si in the medium opposes the phase separation required to enrich the surface with fluorinated segments. A further possible contribution to the contact angle decrease may result from a lower driving force to surface migration for the lower molecular

TABLE II
Advancing and Receding Contact Angle With Water ($\theta_{H_2O\_ADV}$ and $\theta_{H_2O\_REC}$) and Static Contact Angle With *n*-Hexadecane (θ_{C16H34}) Measured on TX*x*CL5Si/SiO_2, GalCL5Si/SiO_2, PCLSi/SiO_2, and SiO_2 after Post-curing Treatment, 2 h at 100°C

Sample Code	$\theta_{H_2O\_ADV}$ (°)	S.D. (°)	$\theta_{H_2O\_REC}$ (°)	S.D. (°)	θ_{C16H34} (°)	S.D. (°)
GalCL5Si/SiO_2	105.5	0.9	95.1	1.0	61.3	0.3
TX1CL5Si/SiO_2	111.6	0.9	101.6	1.0	56.6	0.4
TX2CL5Si/SiO_2	102.3	0.8	89.6	1.7	67.3	0.2
TX3CL5Si/SiO_2	106.5	0.6	97.5	2.1	65.1	0.3
PCLSi/SiO_2	58.0	12.2	54.3	9.5	n.d	n.d.
SiO_2, from TEOS	56.0	3.8	52.4	2.8	n.d	n.d.

t_r = 1 h, reaction time of the sol-gel reaction before coating application; S.D.: standard deviation.

weight of PFPE segments (the decrease of surface tension increases with molecular weight of PFPE). On the other hand, the lower contact angle value for TX3CL5Si/SiO_2 with respect to TX2CL5Si/SiO_2 may be ascribed to both the lower chain mobility (due to the higher molecular weight) and to lower miscibility of the fluorinated oligomer that favors the segregation of PFPE segments in fluorine-rich domains within the solution. These domains can behave like a constraint to the mobility of TX3CL5Si oligomers toward the surface.

When the reaction time before coating application is increased from 1 to 3 h, the overall solution viscosity is increased and the translational chain mobility is decreased; furthermore, as the reaction proceeds, it is expected that the fluorinated copolymers are more and more bonded to siloxane clusters, which is a further reason for the decrease in the migration rate of the PFPE segments to the surface. So it is not surprising that the contact angle values at $t_r = 3$ h are lower than those at $t_r = 1$ h.

This decrease is similar for TX1CL5Si/SiO_2, TX2CL5Si/SiO_2, and GalCL5Si/SiO_2, whereas it is smaller for TX3CL5Si/SiO_2. To explain this different behavior, it can be presumed that in this case a segmental diffusion makes a significant contribution to the PFPE surface enrichment when the solution is applied to the glass substrate, under conditions close to the gel point. As the segmental mobility of constrained PFPE segments is expected to increase with the molecular weight of the PFPE segment, it is easy to see why the above discussed contact angle decrease is lower for TX3CL5Si/SiO_2.

In principle, the segmental mobility of the PFPE segments of GalCL5Si/SiO_2, having a low molecular weight and bonded to the network at one chain end only, should be much higher than those of TX*x*CL5Si/SiO_2, which have crosslinking points at both chain ends. Contrary to what expected, it is worth noting that GalCL5Si/SiO_2 did not show any significant improvement (sometimes a worsening) in terms of non-wettability (extent of surface segregation of the PFPE segments) with respect to the TX*x*CL5Si-based counterparts. The low molecular weight of GalCL5Si, and therefore its high miscibility, may be the reason for the lower contact angles.

The fluorinated hybrid materials were subjected to further heating treatment (2 h at 100°C) in order to evaluate the effect of post-curing on the surface segregation of PFPE segments, and thus on the wettability of the coatings. Contact angle values with water and *n*-hexadecane for ceramers coated after 1 h of sol-gel reaction are reported in Table II. The data show that the applied post-curing treatment leads to hybrids with a markedly improved hydrophobic and oleophobic characteristics (water advancing contact angles = 102–112°; water receding contact angles = 90–102°; *n*-hexadecane contact angles = 57–67°). From that data, it is clear that the curing conditions represent an important parameter for controlling the surface segregation of PFPE segments.

As stated above, a significant change in contact angle values was observed for all investigated samples, but, contrary to what is observed for samples not subjected to post-curing treatment, TX2CL5Si/SiO_2 has the lowest contact angle, whereas the highest one is for TX1CL5Si/SiO_2. Indeed, an increase of contact angle after post-curing is expected for all samples because higher temperature increases the chain mobility and higher reaction time allows for more chains to move to the surface. However, the different increase for different molecular weights of PFPE is not easy to explain, suggesting once more that more complex phenomena are operating.

To obtain a more complete surface characterization, surface tension values of the post-cured coatings were determined together with their dispersive

TABLE III
Total Surface Tension (γ) and Polar (γ^p) and Dispersive (γ^d) Components Measured on TX*x*CL5Si/SiO_2, GalCL5Si/SiO_2, PCLSi/SiO_2, and SiO_2 after Post-Curing Treatment, 2 h at 100°C

Sample Code	γ (mN·m^{-1})	γ^d (mN·m^{-1})	γ^p (mN·m^{-1})
GalCL5Si/SiO_2	16.4	15.0	1.4
TX1CL5Si/SiO_2	16.8	16.5	0.3
TX2CL5Si/SiO_2	15.7	13.2	2.5
TX3CL5Si/SiO_2	15.2	13.8	1.4
PCLSi/SiO_2	41.9	23.5	18.4
SiO_2, from TEOS	42.5	22.6	19.9

t_r = 1 h, reaction time of the sol-gel reaction before coating application.

and polar components (Table III) by applying the Owens and Wendt method to the static contact angle with different probe liquids.

Very low values of surface tension were measured in all cases, with values ranging from 15.2 to 16.8 mN·m^{-1} with an almost negligible contribution from the polar component, in accordance with previously published results for coating systems based on PFPE O-I hybrids.[25] It is interesting to note that the typical value of surface tension for Fluorolink® E is 23 mN·m^{-1},[26] whereas for fully fluorinated PFPE with comparable molecular weight (about 2000 g·mol^{-1}) the value is about 15 mN·m^{-1}, suggesting that the so-called "very surface" of these samples was almost completely composed of PFPE segments, in agreement with previously reported results for similar systems.[25] Surface tension values reported in Table III also indicate that γ values are almost independent of the molecular weight of fluorinated copolymer according to the previously discussed results on wettability (water and *n*-hexadecane contact angles).

Conclusions

Glass substrates were spin-coated with perfluoropolyether-based O-I hybrids prepared by sol-gel process. All the prepared samples presented a strong hydrophobic and oleophobic characteristics (evaluated by measuring the contact angle with water and *n*-hexadecane), almost independently of the molecular weight and of the molecular structure of the fluorinated oligomer. Very low values of surface tension (range = 15–17 mN·m^{-1}) were determined, indicating a strong surface segregation of PFPE segments. Atomic force microscopic analysis revealed the absence of a "Wenzel regime," indicating that the hydrophobic and oleophobic characteristics of the investigated coatings take their origin from the chemical surface composition and, in particular, from the preferential segregation of fluorinated segments on to the outer surface.

The curing conditions play a key role in controlling the surface segregation of PFPE segments. In fact, a post-curing treatment must be applied to obtain hybrids with a very high hydrophobic and oleophobic characteristics. (The maximum values of water advancing angle and *n*-hexadecane contact angle are 112° and 67°, respectively).

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